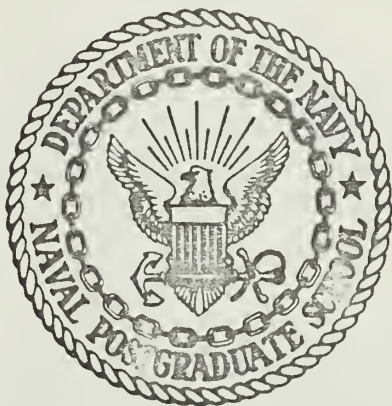


COLLISIONAL DE-EXCITATION RATES FOR THE
FIRST NEGATIVE AND SECOND POSITIVE
SYSTEMS OF NITROGEN

Ronald Francis Walters

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THESIS

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June 1970

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Collisional De-Excitation Rates for the
First Negative and Second Positive Systems of Nitrogen

by

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Lieutenant, United States Navy
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Submitted in partial fulfillment of the
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ABSTRACT

Nitrogen and nitrogen-carbon dioxide gas mixtures were excited by 1.5 MeV protons from a Van De Graaff generator. Intensity versus pressure data were recorded and plotted for the first negative ($\lambda = 3914.4\text{\AA}$) and for the second positive ($\lambda = 3371.3\text{\AA}$) transitions of molecular nitrogen. With the use of theoretical equations and the experimental data, the following reaction rates, k , given in units of $\text{cm}^3\text{-sec}^{-1}$, and collisional de-excitation cross sections, σ , given in units of cm^2 , were calculated: $k = (3.23 \pm 0.92) \times 10^{-10}$, $\sigma = (4.8 \pm 1.3) \times 10^{-15}$ for the de-excitation of the 3914.4\AA N_2 band by N_2 ; $k = (7.40 \pm 0.84) \times 10^{-12}$, $\sigma = (1.09 \pm 0.10) \times 10^{-16}$ for de-excitation of the 3371.3\AA N_2 band by N_2 ; $k = (8.7 \pm 2.0) \times 10^{-10}$, $\sigma = (1.49 \pm 0.33) \times 10^{-14}$ for the de-excitation of the 3914.4\AA N_2 band by CO_2 ; $k = (3.50 \pm 0.22) \times 10^{-10}$, and $\sigma = (5.76 \pm 0.50) \times 10^{-15}$ for the de-excitation of the 3371.3\AA N_2 band by CO_2 .

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I. INTRODUCTION

In a previous study [Ref. 1] molecular nitrogen (N_2) was bombarded by 1.0 to 2.0 MeV protons, and measurements were made to determine the reaction rate coefficient and the de-excitation cross section for the $(N_2)^*$ and $(N_2^+)^*$ bands. In this work, a continuation of that study, an altered experimental procedure was used to verify the same nitrogen reactions as those above and, in addition, to investigate the quenching effect of carbon dioxide (CO_2) on the nitrogen gas system. A constant pressure of 100 torr of N_2 gas was maintained in the reaction chamber and CO_2 was added in increments to a total pressure of 600 torr while measurements were being taken. From a plot of relative intensity versus pressure, experimental determinations were made for the reaction rate coefficient and the de-excitation cross section for the nitrogen first negative transition ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) wavelength ($\lambda = 3914.4 \text{ \AA}$) and the second positive transition ($C^3\Pi_u \rightarrow B^3\Pi_g$) ($\lambda = 3371.3 \text{ \AA}$), where the de-excitation reactions are $(N_2^+)^* + CO_2 \rightarrow N_2 + CO_2^+ + \text{energy}$ and $(N_2)^* + CO_2 \rightarrow N_2 + CO_2^* + \text{energy}$, respectively.

II. EXPERIMENTAL PROCEDURE

A block diagram of the experimental apparatus and associated electronic circuits is illustrated in Fig. 1. A 2.5 MeV Van De Graaff generator was used to accelerate a proton beam down a drift tube. The proton beam passed through a one-half mill aluminum foil window into the reaction chamber where the protons ionized the target gases. The energy loss in passing through the aluminum foil is 0.25 ± 0.05 MeV [Ref. 1].

The reaction chamber is a pyrex glass tee to which is attached a faraday cup which collects proton beam current. The beam current is recorded and integrated by an Eldorado Electronics current integrator, model CI-110, to give continuous readings of beam current and total beam charge. The reaction chamber can be evacuated by a liquid nitrogen trapped oil diffusion pump to 4×10^{-7} torr; this procedure was used for approximately two hours prior to any experimental run.

Also attached to the chamber is an aluminum manifold through which the target gases can be admitted. The pressure in the chamber was measured by two Wallace and Tiernan gauges, one with a 0-50 torr scale and the other with a 0-800 torr scale. The estimated error for these gauges is ± 0.2 torr and ± 5 torr, respectively, as determined by comparison with a liquid oil manometer.

A 15 cm focal length fused quartz lens located 90° from the axis of the proton beam, focuses the reaction spectrum through a mechanical chopper into the 500 micron entrance slits of the Jerral Ash monochrometer. The resolving power of the monochrometer is $\pm 10 \overset{\circ}{\text{\AA}}$ about the central wavelength. The desired spectral line passes into an Electro Optics Associates,

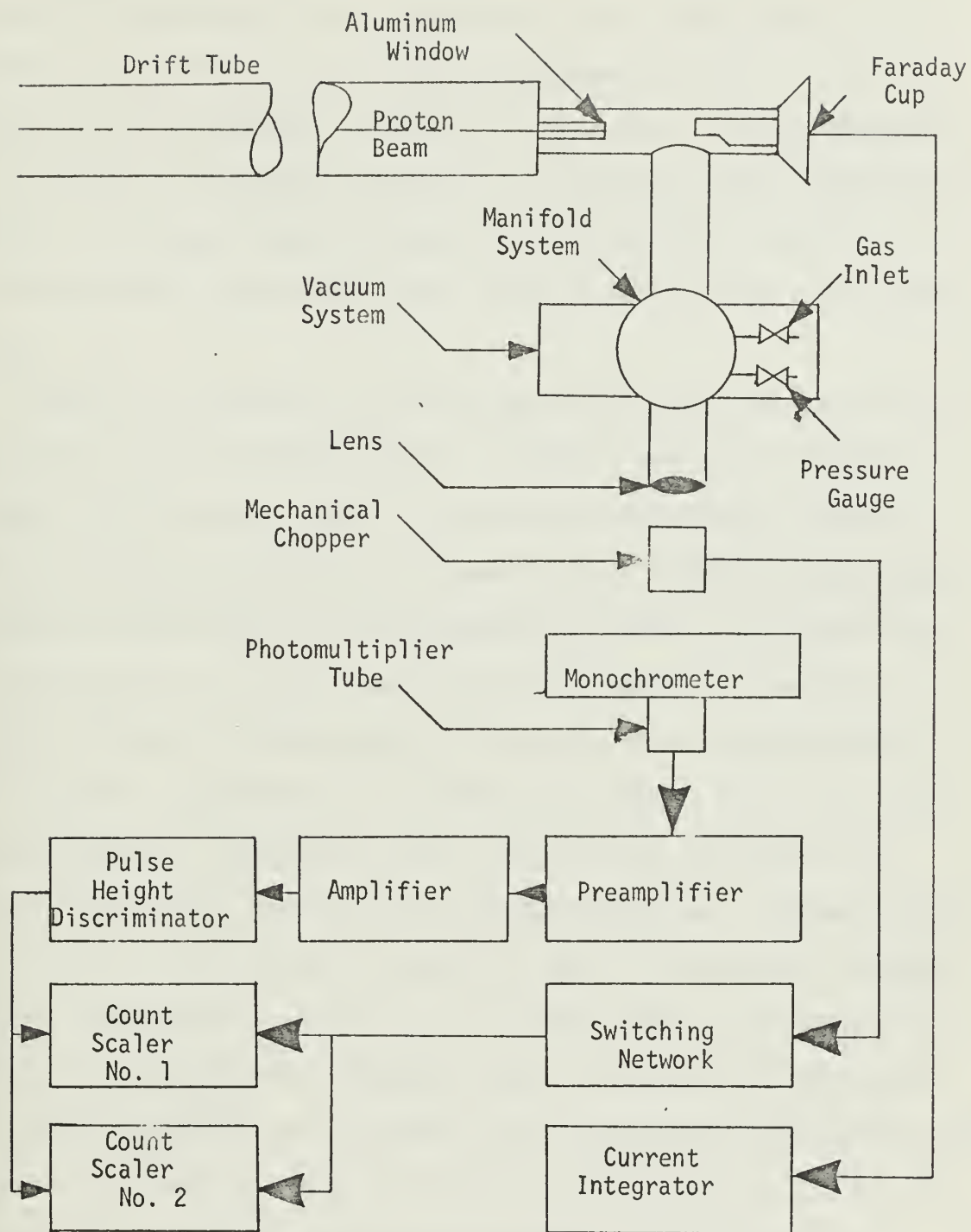


FIGURE 1. Drift Tube, Collision Chamber, and Associated Electronics Diagram

type PM-101 photo multiplier tube assembly with a Dumont 6467 PM tube which has a spectral response peak at approximately 3500 Å. This was ideal for the wavelengths considered in this study. The monochrometer was aligned on the desired wavelength by sending the signal from the PM tube to a Princeton Applied Research lock-in amplifier, model H-8. In this manner the spectral line signal could be peaked prior to an experimental run.

During an experimental run the output signal of the PM tube was sent to an Ortec preamplifier, model 101; a Canberra amplifier, model 810; a Canberra discriminator, model 830; and then to two Canberra scalers. Both scalers were controlled by a transistorized switching network which received an input signal from the mechanical chopper. The scalers were gated such that one scaler counted during the period of time that the PM tube received a light signal, and the other scaler counted during dark periods as determined by the mechanical chopper. Thus one scaler counted photons, background and dark current pulses while the other scaler counted only dark current and background pulses. Another Canberra scaler was pulsed at a rate of one pulse every 0.1 second by a Berkeley double pulse generator, model 903. All three scalers were additionally gated by the beam current integrator, such that, when 50 microcoulombs of proton beam charge were collected, the counting and timing scalers were stopped. The overall system dead time was determined to be 1.7×10^{-6} seconds and appropriate corrections were made to the total count.

The technique in this experiment involved counting individual photons given off by the reacting gases which were nitrogen and nitrogen-carbon dioxide mixtures. From the corrected photon count (NC), the relative intensity (I) of the desired spectral line is calculated as follows:

$$I = \frac{NC}{QB} \quad (1)$$

In equation (1), QB is the total proton beam charge collected. The total corrected count is determined in the following manner:

$$NC = N1 - N2 \quad (2)$$

where N1 is the count of the scaler recording the photon, background and dark current corrected for dead time as follows:

$$N1 = \frac{N1}{[1.0 - (N1 \times 1.7 \times 10^{-6}/T)]} \quad (3)$$

In equation (3) N1 is the count on the scaler and T is the counting period in seconds. N2 is the count of the scaler recording dark current and background corrected in a similar manner. The average background current was approximately 25 counts per second, but was found to vary and thus a point to point correction was applied. The PM tube was cooled with crushed carbon dioxide and liquid nitrogen to reduce dark current.

Care was taken to insure that the counting rate remained below 20,000 counts per second. The counting rate was varied by changing the beam current. The spectral intensity is independent of the beam current, in that the number of interactions is dependent only on the number of protons, the energy of the protons and the pressure and temperature of the reacting molecules. The proton energy was constant at 1.5 MeV throughout the experiment, and for any one count period the pressure was constant. The temperature of the reacting molecules is assumed to remain constant. The value of QB was fixed at 50 microcoulombs of charge and thus the counting period was dependent on the time required to collect this charge.

The 500 micron slits of the monochrometer were perpendicular to the proton beam path and the monochrometer was positioned such that light 1

to 2 mm from the aluminum window passed to the PM tube. In this region, energy loss is small and the energy of the protons is more or less pressure independent.

At the outset of this experiment, attempts were made to photograph the spectrum of carbon dioxide from 2000-7000 Å where the carbon dioxide molecules were excited by 1.6 MeV protons. A Gaertner L 254 quartz spectrometer and 70 mm Kodak 2485 high speed film were used. The carbon dioxide spectrum was not recorded on the film for exposure times in excess of three hours. An attempt was made to enhance the carbon dioxide spectrum by mixing 50 torr of carbon dioxide with 500 torr of helium. Protons in the energy range of 1.7 MeV were used as the exciting particles. A very weak carbon dioxide vibration-rotation spectrum was obtained for an exposure time in excess of three hours. Smelley [Ref. 1] reported excellent results in photographing the nitrogen spectrum and noted that the 3371.3 Å wavelength and 3914 Å wavelength lines were the most intense.

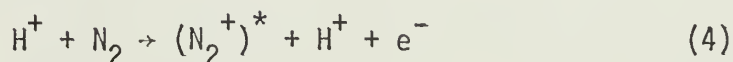
The standard experimental procedure was to admit research grade nitrogen into the reaction chamber in increments to a pressure of 100 torr while pressure and intensity data were recorded. At this point carbon dioxide was added to the reaction chamber to a total pressure of 600 torr and again, pressure and intensity data were recorded.

An IBM 360 computer was used for data reduction, theoretical calculations and curve plotting. Figures 2 and 3 are typical results of pressure versus intensity for the nitrogen first negative and second positive systems for pressures up to 100 torr. Figures 4 and 5 are indicative of the results achieved using 100 torr nitrogen and a balance CO₂ up to a pressure of 600 torr.

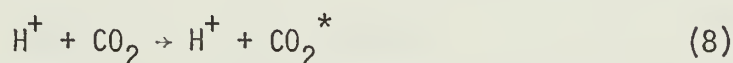
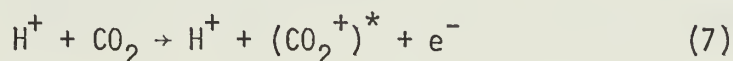
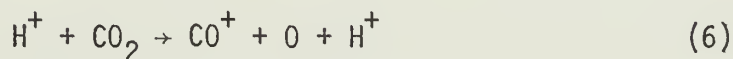
III. THEORY

A. BACKGROUND

The primary nitrogen excitation reactions occurring in the collision chamber upon proton (H^+) impact for the lines studied in this research are:



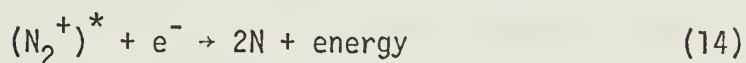
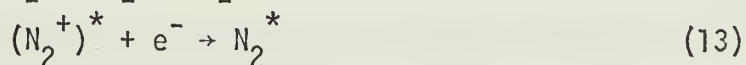
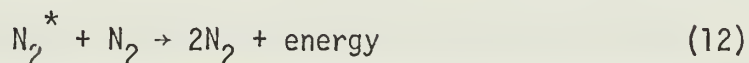
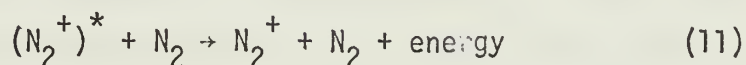
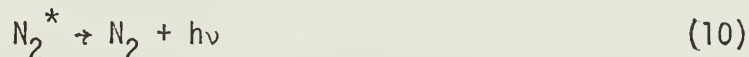
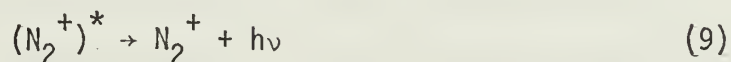
The primary carbon dioxide excitation reactions expected to occur are:



These latter three reactions are believed to proceed with a considerably lower probability than the nitrogen excitation reactions, because of the difficulty of obtaining a carbon dioxide spectrum on photographic plate, whereas the nitrogen spectrum was easily photographed. Dibeler, et al. [Ref. 2] has shown that dissociation of carbon dioxide as in equation (6) starts to occur at about 19.5 eV. Also, one might expect some excited states of CO^+ , atomic oxygen (O) and molecular oxygen (O_2); however, these were not observed in the attempts to photograph the CO_2 spectrum. Additionally, McCorkey et al. [Ref. 3] using 160 eV electrons for excitation of CO_2 noted no presence of excited atomic or molecular species, such as C^* , CO^* , O_2^* , or $(O_2^+)^*$. Thus if these reactions occur, the reaction rates are assumed to be negligible in comparison with the rates of equations (6), (7) and (8) and may be disregarded in the excitation process. Equation (7) is certainly a reasonable reaction upon H^+ impact. Al Joboury et al. [Ref. 4] have established that the ground

state of the ion CO_2^+ is at about 13.8 eV, and additional excited states exist at 17.3, 18.1 and 19.4 eV. More recently Judge et al. [Ref. 5] have reported on extensive identification and classification of the excited states of CO_2^+ .

The primary de-excitation reactions of the nitrogen first negative and second positive systems are:



The de-excitation mechanisms of the two nitrogen systems in the presence of CO_2 are given in a later section.

The general rate equation [Ref. 6], given below as equation (15), with modifying assumptions was used to develop a set of equations from which the collisional de-excitation rate and the reaction cross section could be computed.

$$\frac{dN_k^*}{dt} = p v N \sigma_k + \sum_{\ell > k} \lambda_{\ell k} N_{\ell}^* - \sum_{k > i} \lambda_{ki} N_k^* - \sum_j N_k^* K_j n_j + \sum_m n_m^* K_m n_k \quad (15)$$

In equation (15) the first term is direct excitation to state k by protons given in terms of the excitation cross section σ_k , proton beam density p , target density N and proton velocity v . The second term accounts for transitions from higher excited state ℓ into state k given in terms of the transition probability $\lambda_{\ell k}$ of decay from state ℓ into

state k , and N_{ℓ}^* the number density of excited particles in state ℓ . The third term is the radiative loss by transitions from state k to a lower state i . This is given in terms of the transition probability λ_{ki} , and N_k^* the number density of excited particles in state k . The fourth term accounts for the collisional de-excitation rate k with particles n_j . The terms here are the collisional de-excitation rate K_j , the density of excited particles N_k^* , and n_j the density of particles of type j . The fifth term is the excitation to state k by collisions with atoms or molecules in excited state n_m^* . This term is temperature dependent and accounts only for those excited particles which have reached thermal equilibrium with the target particles. It is given in terms of density of particles in excited state n_m^* , the collisional excitation reaction rate K_m , and n_k , the density of target particles involved in collisional excitation reactions.

In the first term the excitation cross section σ_k is energy dependent, but energy was held constant throughout the experiment; thus, σ_k is a constant. For any given data run, the proton beam density p and the velocity v were held constant and the target gas density was also constant; thus, the first term is constant.

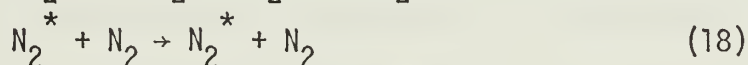
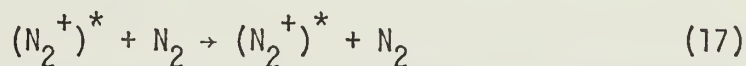
$$pvN\sigma_k = R_k \quad (16)$$

It was assumed that R_k is proportional to pressure (P) in the target chamber.

In the second term, states above state k can be populated by direct interaction with the protons. These higher lying states can then decay to state k and thus serve as an additional mechanism for excitation to state k . These excitation processes were also assumed to be proportional to pressure, and thus, are considered additive to the first term. Later analysis of the data justifies this assumption.

In the third term it was assumed that $\sum_k \lambda_{ki} = \lambda$ a constant for the spectral line under study. Additional assumptions are that in the fourth term $\sum_j K_j = K$ a constant for the line in question, and that n_j the number density of particles of type j is proportional to the partial pressure of the particles of type j . This assumption follows directly from the ideal gas law which is valid in the pressure ranges used in this study [Ref. 7]. It was also assumed that the number density of particles in excited state k , N_k^* , is proportional photo current intensity (I).

In the fifth term two separate conditions apply. For proton bombardment on molecular nitrogen alone, the excited species n_m^* will be either $(N_2^+)^*$ or N_2^* depending on which line is under observation. The unexcited species N_k will be N_2 in both cases. Thus the possible collision mechanism will be:



In either reaction the net result is no change in the excited or unexcited species and the term can be neglected. As noted earlier, the fifth term applies only to those excited species which have kinetic energies given by the Boltzman distribution which is assumed to hold in the reaction chamber. In the case of nitrogen-carbon dioxide mixtures in the reaction chamber, the term is neglected because of the marked reduction in intensity with carbon dioxide present. If the carbon dioxide excited species at reaction chamber temperatures transferred its energy to nitrogen, one would observe an enhancement of the nitrogen spectrum.

Under conditions of equilibrium where excitation to state k is equal to de-excitation from state k , and after applying the above assumptions,

the general rate equation becomes:

$$\frac{dN_k^*}{dt} = 0 = R_k - \lambda N_k^* - K_j n_j N_k^* \quad (19)$$

or

$$aP = \lambda bI + K_j \frac{b}{kT} PI \quad (20)$$

$$P = \frac{\lambda b}{a} I + \frac{K_j b}{a kT} PI \quad (21)$$

$$P = AI + BPI \quad (22)$$

where the ideal gas law at constant volume is $P_j = n_j kT$, and as noted before, the assumptions are made that $R_k = aP$ and $N_k^* = bI$. Thus one has $A = \frac{\lambda b}{a}$ and $B = \frac{K_j b}{a kT}$.

B. NITROGEN AS THE TARGET GAS

Equation (22) in a modified form is suggestive of an experimental means of determining the unknown constants A and B.

$$\frac{P}{I} = A + BP \quad (23)$$

By plotting P/I versus P , a straight line should result with the intercept giving the value of A and the slope giving the value of B. As shown in Figs. 6 and 7, this was the case for pressures below 100 torr. For pressures above 100 torr, a deviation from the linear relationship was observed which is attributable to secondary processes in the reaction chamber [Ref. 1]. In all cases the pressure for pure nitrogen was varied from 0 to 100 torr and with the aid of an IBM 360 computer, equation (23) was solved by curve fitting techniques.

By taking the ratio of B to A the reaction rate, K_j , can be determined.

$$K = \frac{BkT}{A \tau} \quad (24)$$

In equation (24), the radiative lifetime, τ , is the reciprocal of the decay probability λ . Bennet and Dalby [Ref. 8] experimentally determined the radiative lifetimes for nitrogen and these values were used in this experiment. The values are $\tau = 6.58 \times 10^{-8}$ secs for the first negative (3914\AA) system and $\tau = 4.45 \times 10^{-8}$ secs for the second positive (3371\AA) system of nitrogen. A dimensional analysis of equation (23) after conversion shows A to be in units of sec-cm^{-3} and B to be in units of sec-erg^{-1} which is consistent with equation (24).

The calculation of the collisional de-excitation cross section (σ_d) for the case of nitrogen de-exciting nitrogen can be made by noting $N^* K_j n_j = N^* \sigma_d \phi_j$ where ϕ_j is the flux of particles of type j. Also $\phi_j = \bar{V}_r n_j$ where \bar{V}_r is the mean relative velocity between the particles. Thus, one has

$$N^* K_j n_j = N^* \sigma_d n_j \bar{V}_r \quad (25)$$

$$\sigma_d = K_j / \bar{V}_r \quad (26)$$

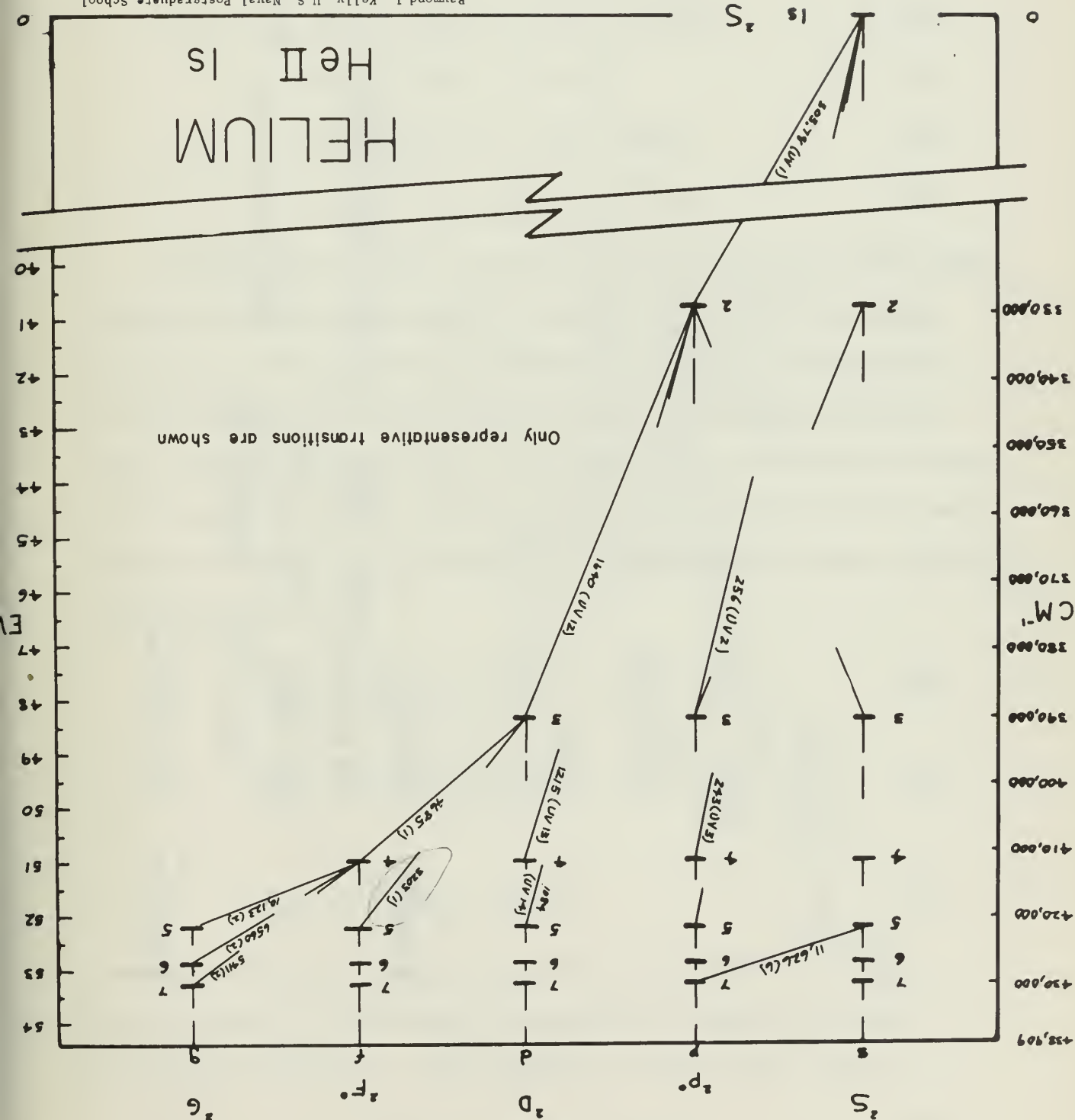
where

$$\bar{V}_r = \left[\frac{8kT}{\pi} \frac{(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \quad (27)$$

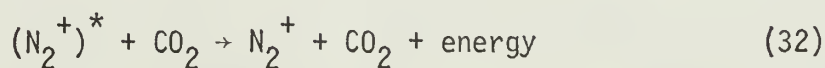
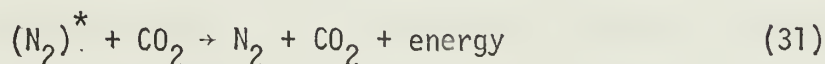
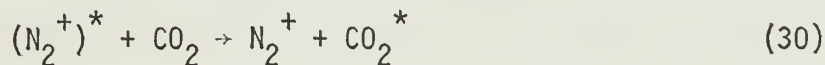
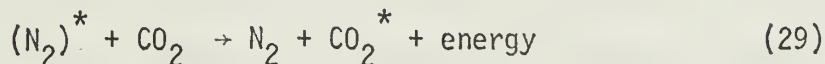
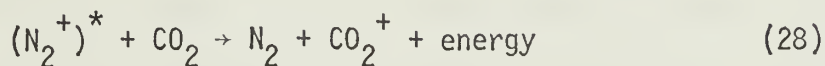
for a mixture of two gases in equilibrium.

C. NITROGEN WITH CARBON DIOXIDE

The initial experimental results of nitrogen and carbon dioxide mixtures shown in Figs. 4 and 5 indicate that the presence of carbon dioxide acts to quench the $(N_2)^*$ and $(N_2^+)^*$ states by a much larger collisional de-excitation rate than that obtained with nitrogen alone.



The de-excitation reactions of the $(N_2^+)^*$ and $(N_2)^*$ systems are as in equations (9), (10), (11) and (12) as well as by:



As noted earlier direct excitation of the carbon dioxide under proton impact is believed to proceed at a much lower rate than the nitrogen reactions, and CO_2 excitation reactions are neglected. Secondary de-excitation mechanisms such as photon absorption by carbon dioxide are also assumed to be negligible. Thus the primary de-excitation mechanism of nitrogen with carbon dioxide present is assumed to be by collisional energy transfer. Using the general rate equation with the same assumptions as before one has:

$$R_k = \lambda_{ki} N_k^* + N_k^* (K_j^{N_2} n_j^{N_2} + K_j^{CO_2} n_j^{CO_2}) \quad (33)$$

$$aP_{N_2} = \lambda bI + bI \left[\frac{(K_j^{N_2} P_j^{N_2})}{kT} + \frac{K_j^{CO_2} P_j^{CO_2}}{kT} \right] \quad (34)$$

$$P_{N_2} = AI + (BP_{N_2} + EP_{CO_2})I \quad (35)$$

where the constants A and B are as before, the constant $E = \frac{bK^{CO_2}}{akT}$, and P_{N_2} and P_{CO_2} are the partial pressures of nitrogen and carbon dioxide, respectively. A rearrangement of equation (35) yields:

$$E = [P_{N_2} - (A + BP_{N_2})I / P_{CO_2} I] \quad (36)$$

The value of E was determined experimentally by first recording pressure versus intensity for 100% nitrogen, as noted earlier, up to a pressure of 100 torr. The values of A and B were then calculated. This procedure was used for each experimental run as the values of A and B varied from run to run, however, the ratio of B/A remained invariant to within experimental error. Then industrial grade carbon dioxide with a purity of 99.9% was added to a total pressure of 600 torr, and again pressure versus intensity data were recorded. In equation (36) the values of A, B, and P_{N_2} are known and $P_{CO_2} = P - P_{N_2}$. The only variables are then intensity I and total pressure P. An IBM 360 computer was then used to calculate the value of E from equation (36) and to plot the experimental results. Figures 4 and 5 are typical results of pressure versus intensity for the case of carbon dioxide - nitrogen mixtures.

By rearranging equation (36) one has:

$$I = P_{N_2} / [(A + BP_{N_2}) + EP_{CO_2}] \quad (37)$$

Using equation (37) and the value of E determined experimentally, intensities at various pressures were calculated and a theory curve was superimposed on the experimental points. A comparison of the predicted intensities both numerically and graphically as in Figs. 4 and 5 shows good correlation between experiment and equation (36).

The collisional de-excitation reaction rate for carbon dioxide K_{CO_2} can be calculated as follows:

$$E = \frac{bK_{CO_2}}{aKT} \quad (38)$$

$$K_{CO_2} = E/A \frac{kT}{\tau} \quad (39)$$

where the value of A was substituted in equation (38). Also by analogy

with equation (26), the collisional de-excitation cross section for carbon dioxide σ_{CO_2} is:

$$\sigma_{\text{CO}_2} = K_{\text{CO}_2} / \bar{Vr} \quad (40)$$

where \bar{Vr} is given by equation (27) and the masses m_1 and m_2 are the masses of nitrogen and carbon dioxide, respectively.

IV. RESULTS

A. GENERAL

Table I is a summary of the results obtained in this research for the collisional de-excitation reaction rates and the respective cross sections. Values obtained by Smelley [Ref. 1] for the nitrogen de-excitation reactions are included for comparison. Recently Mitchell [Ref. 9] has published results for the same nitrogen systems. Mitchell used monochromatic x-rays in the 0.9 to 8.0 KeV energy range to excite the nitrogen gas. For the collisional de-excitation by nitrogen, Mitchell obtained reaction rates of $4.53 \times 10^{-10} \text{ cm}^3 - \text{sec}^{-1}$ for the first negative transition and 1.12×10^{-11} for the second positive transition. The values obtained in this research agree to within experimental uncertainty of those obtained by Smelley.

A search through the current literature revealed no data concerning the nitrogen-carbon dioxide collisional de-excitation reactions.

Both Smelley and Mitchell in the references cited above calculated the reaction rates of the first negative and second positive nitrogen systems using oxygen as the quencher, and the values calculated are included in Table I. A comparison of these values indicates that the collisional de-excitation of nitrogen in the presence of oxygen and carbon dioxide proceeds at comparable rates.

B. DISCUSSION

The assumptions made in arriving at equation (23) seem to be valid in light of the close correlation between the experimental results and the theoretical equations. Secondary excitation effects, such as excitation by high energy electrons and soft x-rays, were neglected in

Transition	3914 Å N_2 + N(0-0)	3371 Å N_2 2P(0-0)
K_{N_2} (cm ³ -sec ⁻¹)	$(3.23 \pm 0.92) \times 10^{-10}$	$(7.40 \pm 0.84) \times 10^{-12}$
K_{CO_2} (cm ³ -sec ⁻¹)	$(8.70 \pm 2.0) \times 10^{-10}$	$(3.50 \pm 0.22) \times 10^{-10}$
$\sigma_d(N_2)$ cm ²	$(4.80 \pm 1.3) \times 10^{-15}$	$(1.09 \pm 0.06) \times 10^{-16}$
$\sigma_d(CO_2)$ cm ²	$(1.49 \pm 0.33) \times 10^{-14}$	$(5.76 \pm 0.05) \times 10^{-15}$
K_{N_2} [Ref. 1]	$(2.19 \pm 0.29) \times 10^{-10}$	$(7.11 \pm 1.64) \times 10^{-12}$
$\sigma_d(O_2)$ [Ref. 1]	$(3.25 \pm 0.45) \times 10^{-15}$	$(1.06 \pm 0.25) \times 10^{-16}$
K_{O_2} [Ref. 1]	$(5.70 \pm 0.80) \times 10^{-10}$	$(4.62 \pm 0.67) \times 10^{-10}$
K_{O_2} [Ref. 9]	7.36×10^{-10}	3.12×10^{-10}

TABLE I. Reaction Rates (K) and De-Excitation Cross Sections (σ_d)

arriving at equation (23). It was assumed that the only excitation processes were direct, and that this was proportional to the pressure of the target gas. The results shown in Figs. 6 and 7 seem to bear this out convincingly in the region from 1 to 100 torr, where a linear relationship holds as predicted by equation (23).

In the development of the pressure versus intensity relationship for nitrogen-carbon dioxide mixtures, it was assumed that direct excitation of carbon dioxide was negligible and that carbon dioxide quenches the $(N_2)^*$ and $(N_2^+)^*$ states by a much larger collisional de-excitation rate than does nitrogen. The pressure versus intensity relationship for the $3914\text{\AA } N_2^+$ transition is shown in Fig. 3. It is observed that at approximately 30 torr, the rate of increase in intensity approaches zero and this situation prevails to a pressure of 100 torr. In Fig. 5, the pressure versus intensity relationship for the same transition is shown after the introduction of carbon dioxide. At a carbon dioxide partial pressure of 50 torr, the intensity has decreased by a factor of 2. This marked decrease in intensity continues to a total pressure of approximately 300 torr. The same observations can be made for the $3371\text{\AA } N_2$ transition. As in the case for pure nitrogen de-excitation, it appears that the assumptions made in the nitrogen-carbon dioxide reactions are valid to a high degree as evidenced by the agreement between the predicted and experimental results.

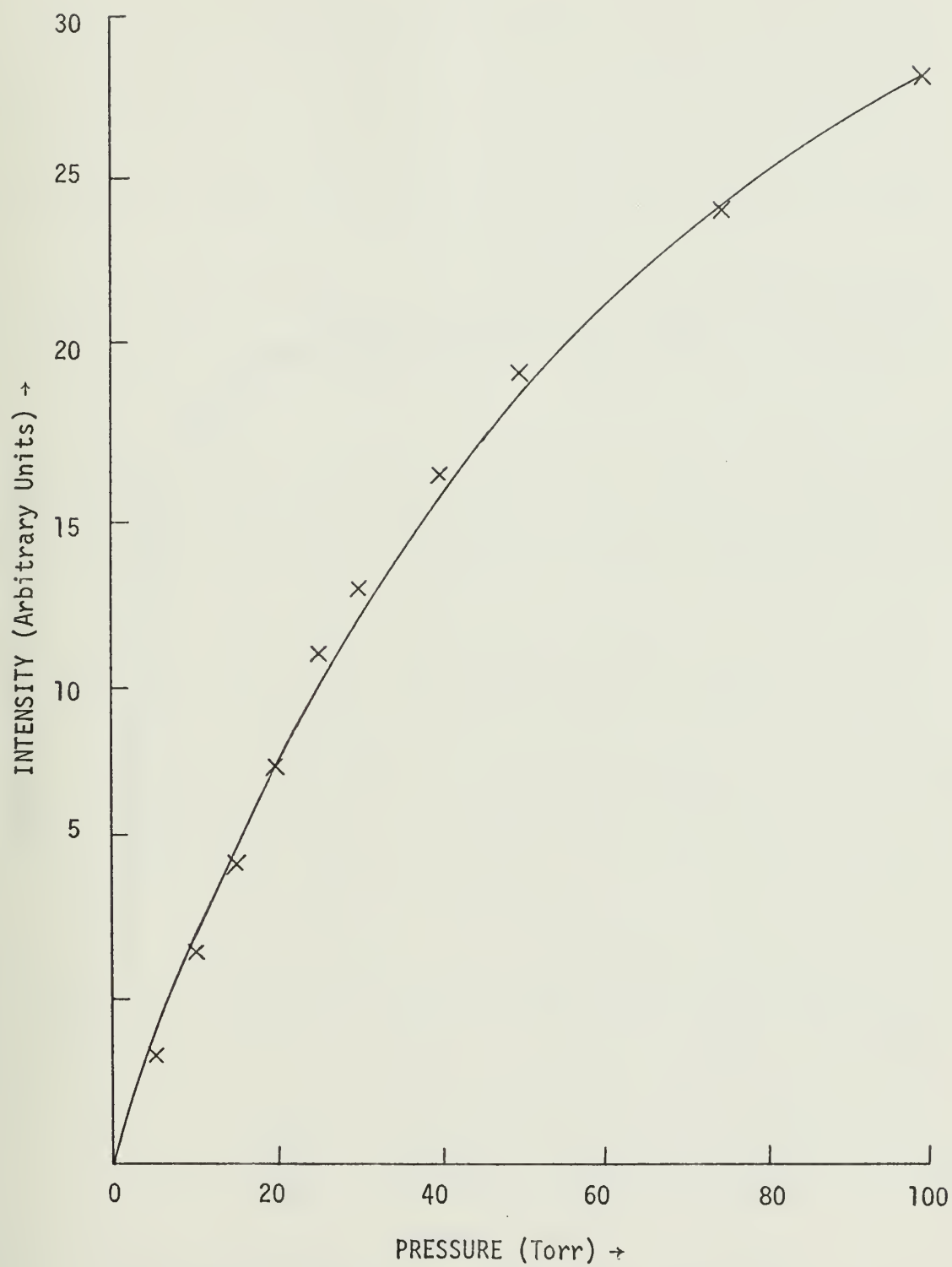


FIGURE 2. Intensity versus Pressure (3371\AA). H^+ on N_2 .

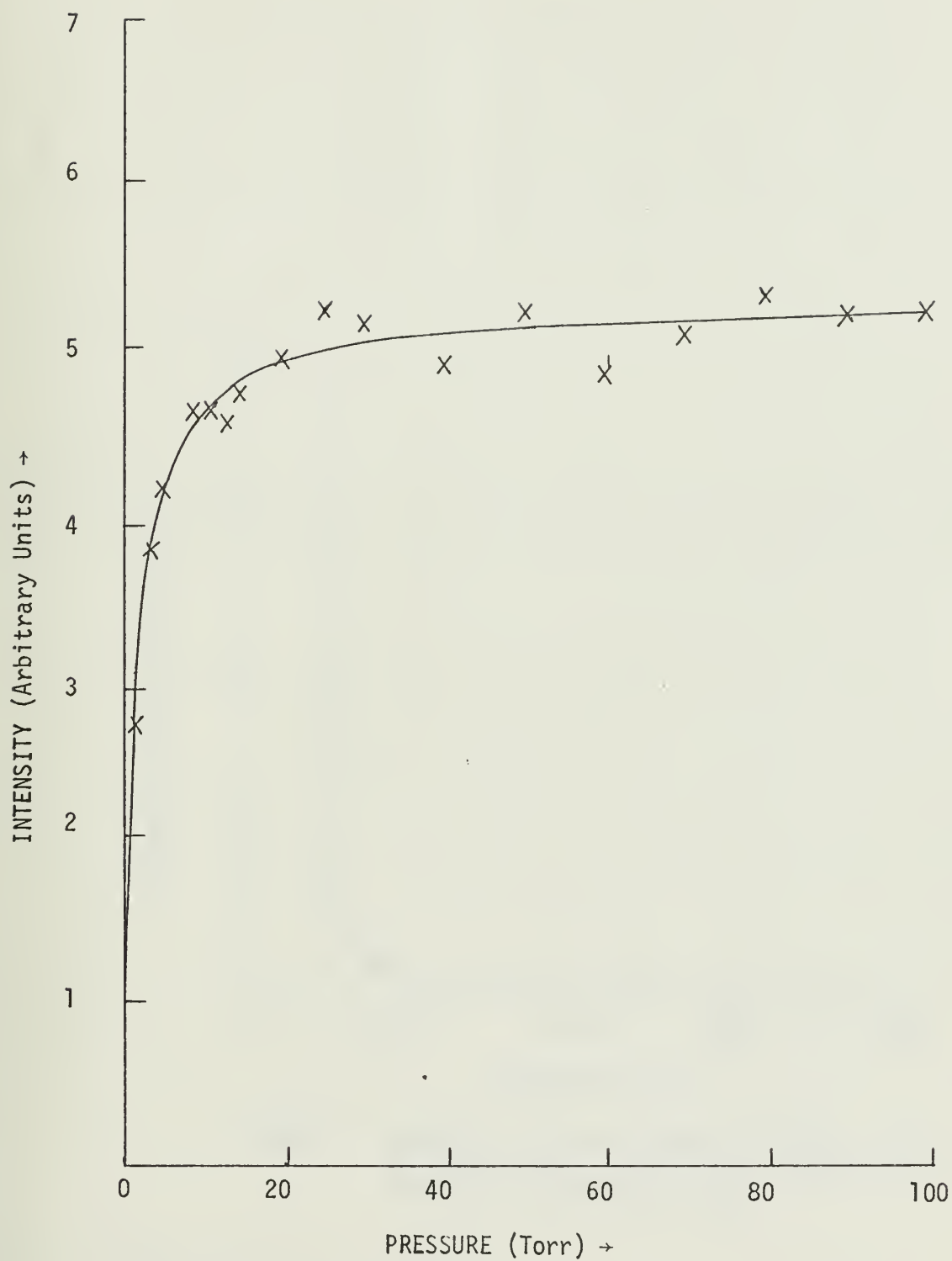


FIGURE 3. Intensity versus Pressure (3914\AA). H^+ on N_2 .

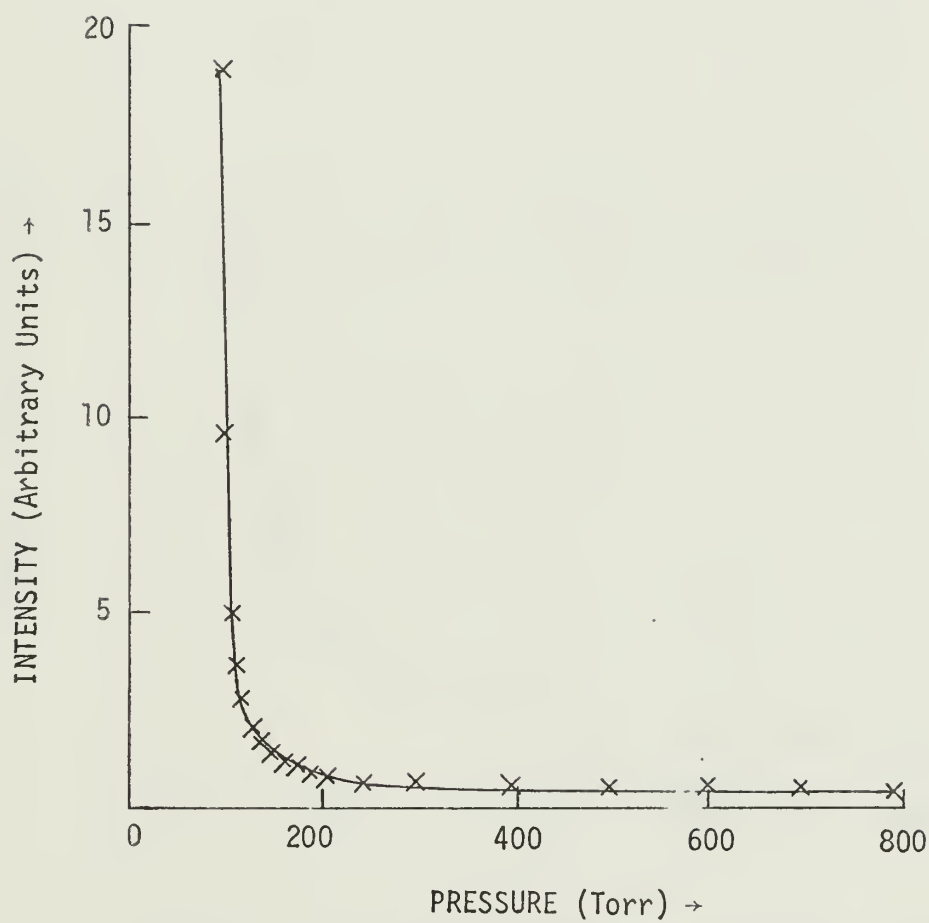


FIGURE 4. Intensity versus Pressure (3371\AA). H^+ on 100 Torr N_2 , Balance CO_2 . Experimental Data (x), Theory Comparison.

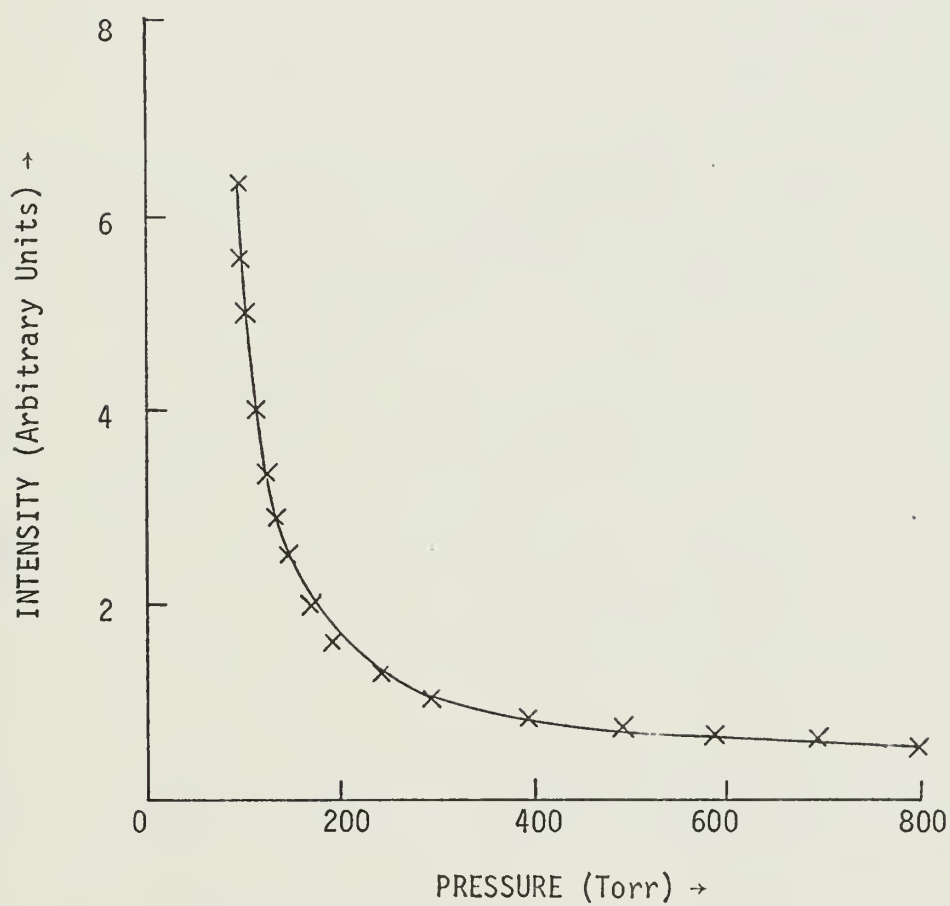


FIGURE 5. Intensity versus Pressure (3914\AA). H^+ on 100 Torr N_2 , Balance CO_2 . Experimental Data (x), Theory Comparison.

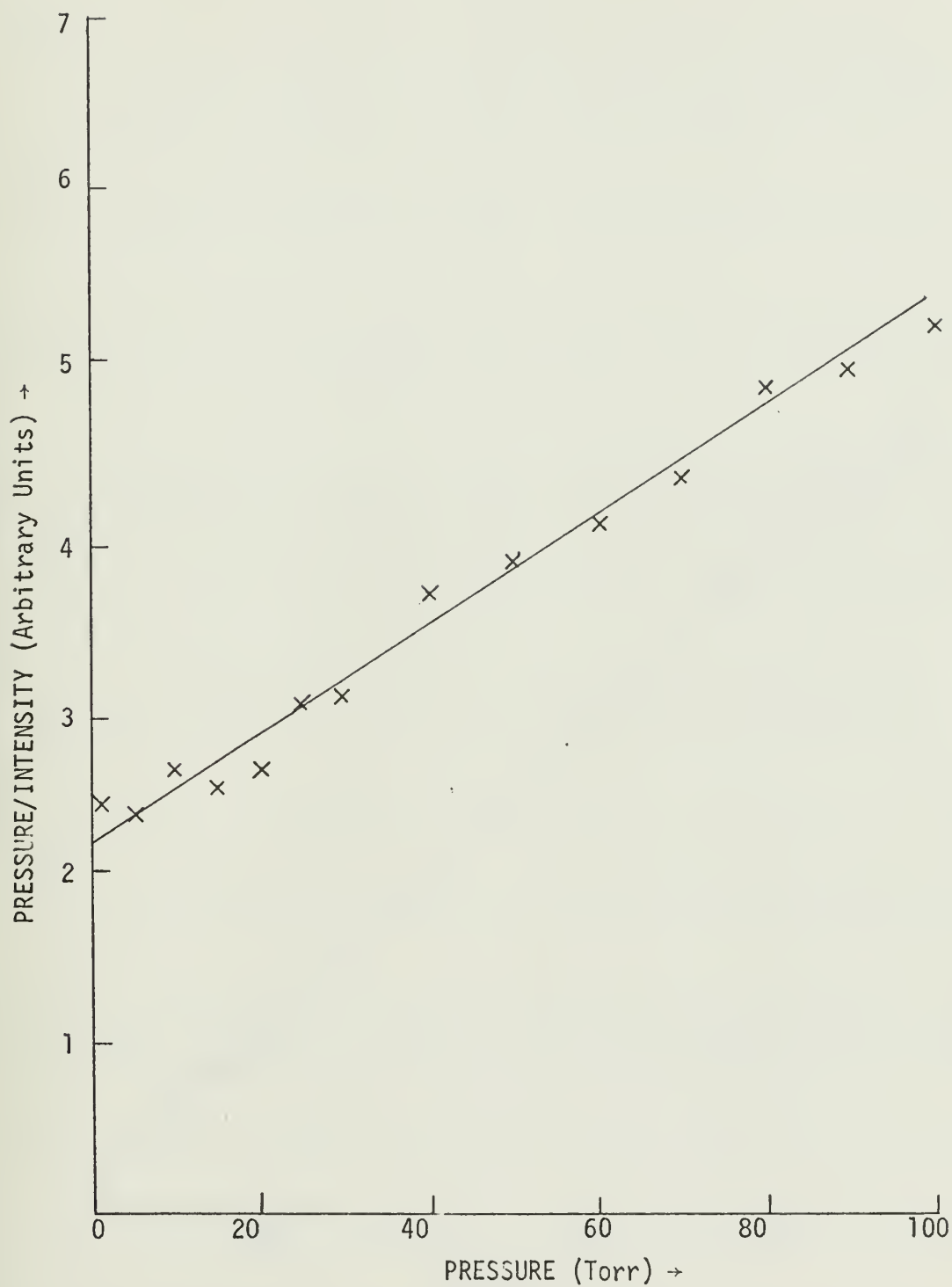


FIGURE 6. Pressure/Intensity versus Pressure (3371\AA).
 H^+ on N_2 .

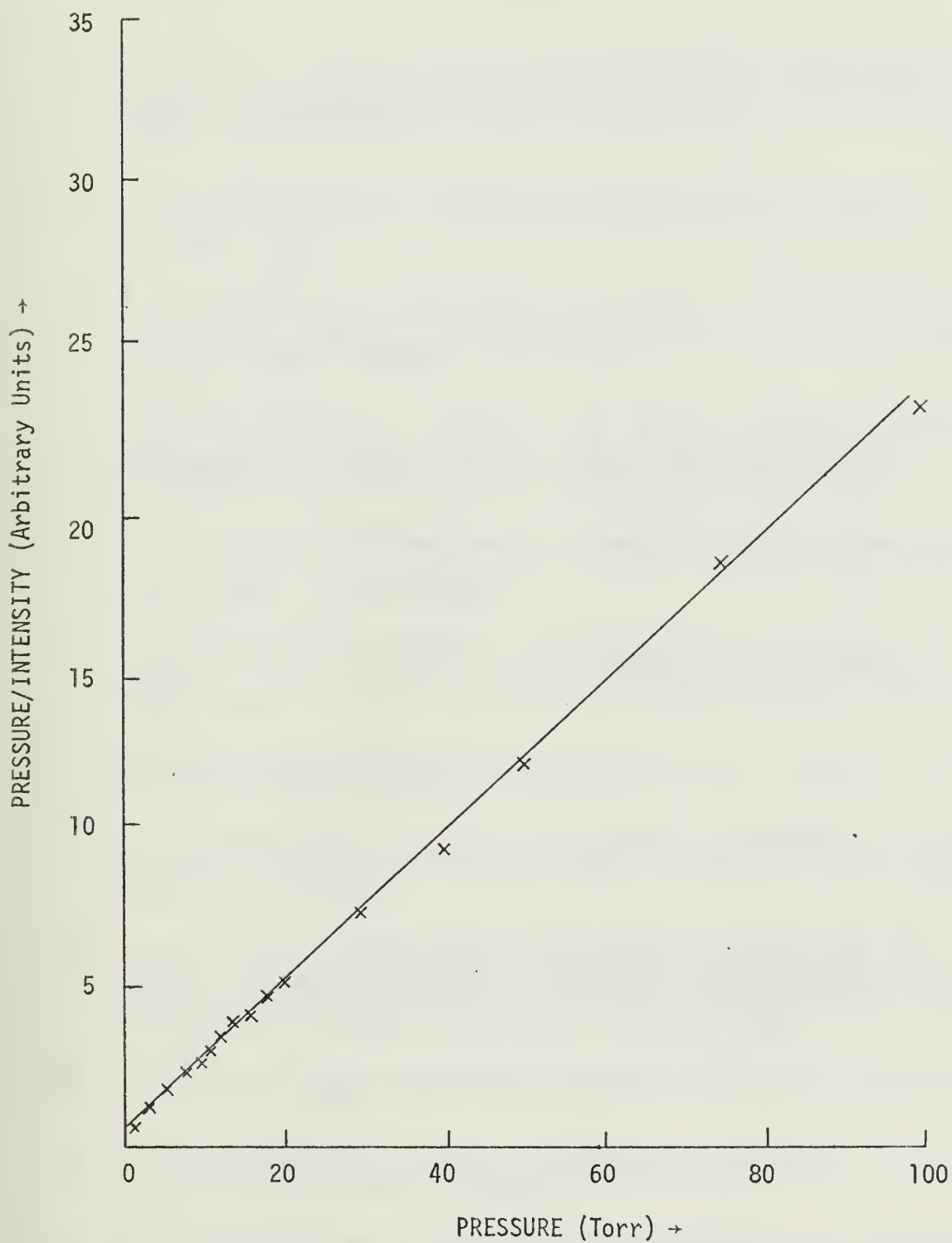


FIGURE 7. Pressure/Intensity versus Pressure (3914Å). H^+ on N_2 .

BIBLIOGRAPHY

1. A. R. Smelley, Reaction Rates for the Collisional De-Excitation of the $B^2\Sigma^+$ State of N_2 and the $C^3\Pi_u$ State of N_2 , Naval Postgraduate School, Thesis (1969).
2. V. H. Dibeler and J. A. Walker, "Mass-Spectrometric Study of Photoionization. VI. O_2 , CO_2 , COS , and CS_2 ," J. Opt. Soc. Am. **57**, 1007 (1967).
3. J. W. McConkey, D. J. Burns and J. M. Woolsey, "Absolute Cross Sections for Ionization and Excitation of CO_2 by Electron Impact," Proc. Phys. Soc. (London). **1**, 71 (1968).
4. M. I. Al-Joboury, D. P. May and D. W. Turner, "Molecular Photoelectric Spectroscopy. Part IV. The Ionization Potentials and Configuration of Carbon Dioxide, Carbon Oxysulphide, Carbon Disulphide, and Nitrous Oxide," J. Chem. Soc. 6350 (1965).
5. D. L. Judge, G. S. Bloom, and A. L. Morse, "Studies of the CO_2^+ [$A^2\Pi_u \rightarrow X^2\Pi_g$] Bands Using Photon Excitation from the Neutral Molecule," Can. J. Phys. **47**, 489 (1969).
6. C. A. Blank (Project Officer). DASA Reaction Rate Handbook, Santa Barbara: DASA Information and Analysis Center, General Electric, TEMPO, 1967.
7. M. N. Zemansky, Heat and Thermodynamics, 4th ed., New York: McGraw-Hill Book Company, 1957.
8. R. G. Bennett and F. W. Dalby, "Experimental Determination of the Oscillator Strength of the First Negative Bands of N_2^+ ," J. Chem. Phys. **31**, 434 (1959).
9. K. B. Mitchell, Fluorescence Efficiencies and Collisional Deactivation Rates for N_2 and N_2^+ , Excited from Deposition of Soft X-Rays, Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico, 3 November 1969.
10. D. R. Bates, Atomic and Molecular Processes, New York, Academic Press, Inc., 1962.
11. G. Herzberg, Molecular Spectra and Molecular Structure, 2nd ed., New York, D. Van Nostrand Company, Inc., 1950.
12. R. W. B. Pearse and A. G. Gaydon, The Identification of Molecular Spectra, 3rd ed., New York, John Wiley and Sons, Inc., 1963.

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13. ABSTRACT Nitrogen and nitrogen-carbon dioxide gas mixtures were excited by 1.5 MeV protons from a Van De Graaff generator. Intensity versus pressure data were recorded and plotted for the first negative ($\lambda=3914.4\text{\AA}$) and for the second positive ($\lambda=3371.3\text{\AA}$) transitions of molecular nitrogen. With the use of theoretical equations and the experimental data, the following reaction rates, k , given in units of $\text{cm}^3\text{-sec}^{-1}$, and collisional de-excitation cross sections, σ , given in units of cm^2 , were calculated: $k=(3.23 \pm 0.92) \times 10^{-10}$, $\sigma=(4.8 \pm 1.3) \times 10^{-15}$ for the de-excitation of the 3914.4\AA N_2^+ band by N_2 ; $k=(7.40 \pm 0.84) \times 10^{-12}$, $\sigma=(1.09 \pm 0.10) \times 10^{-16}$ for de-excitation of the 3371.3\AA N_2 band by N_2 ; $k=(8.7 \pm 2.0) \times 10^{-10}$, $\sigma=(1.49 \pm 0.33) \times 10^{-14}$ for the de-excitation of the 3914.4\AA N_2 band by CO_2 ; $k=(3.50 \pm 0.22) \times 10^{-10}$, and $\sigma=(5.76 \pm 0.50) \times 10^{-15}$ for the de-excitation of the 3371.3\AA N_2 band by CO_2 .			

KEY WORDS	LINK A		LINK B		LINK C	
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